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PINONIC ACID,
A New Chemical for Industry

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PREFACE

The principal purpose of this publication is to apprise industry of opportunities for profitable new commercial ventures arising from research conducted by USDA's Agricultural Research Service on naval stores products. In addition, it provides a medium through which the Southern Utilization Research and Development Division can better serve the naval stores industry and, in return, receive practical guidance for future research designed to benefit agriculture, processors, and the consumer.

PINONIC ACID,,

A New Chemical for Industry

by

G. W. Hedrick, G. S. Fisher, R. V. Lawrence,
and L. W. Mazzeno, Jr.

INTRODUCTION

Pinonic acid is a versatile chemical that can be prepared easily by the oxidation of alpha-pinene with potassium permanganate or ozone. The preparation of pinonic acid from alpha-pinene provides a means for increasing markets of naval stores products. Alpha-pinene, the principal component of turpentine, exists in proportions ranging from 50 to 80 percent. It has been estimated that the US naval stores industry is capable of producing at least 1.6 million barrels (50 gallons each) of turpentine annually, a production output approximately 2.5 times that realized in 1960.^{2/} This potential accounts for the entire productivity of the three segments comprising the naval stores industry: gum, wood, and sulfate. The extent to which the potential can be realized through the coming years will depend upon the success achieved in extending present markets through low cost production of high quality products and through the development of new markets through research and application studies.

This report affords a brief description of the processes for the production of pinonic acid; lists its properties, its potential uses, and production costs so that industry may avail itself of the opportunity for diversifying naval stores markets by the production of a versatile, useful, and inexpensive chemical intermediate.

PROPERTIES

Name: Pinonic acid (3-acetyl-2, 2-dimethylcyclobutane acetic acid)

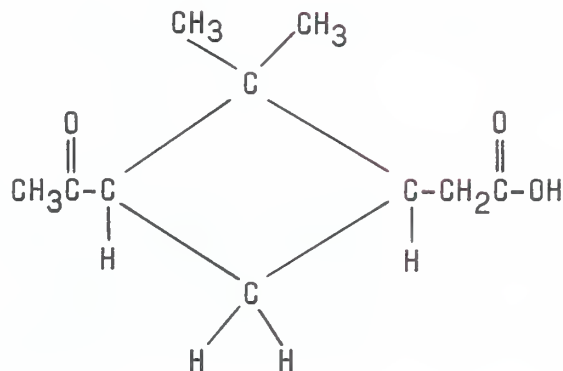


Figure 1. --Structure of pinonic acid.

Formula: C₁₀H₁₆O₃
Appearance: Colorless crystals
Neutral equivalent: 184.13
Melting point: 105° C.
Solvents: Water, acetone, ether, chloroform, benzene; sparingly soluble in aliphatic solvents.
Chemical properties: Pinonic acid contains a carboxyl and methyl carbonyl moiety. Its reactions are governed to a high degree by the presence of these reactive groups.

POSSIBLE USES OF PINONIC ACID

Pinonic acid is a versatile chemical and can be converted to many derivatives including dibasic acids, glycols, and monomers, some of which possess unusually outstanding thermal stability.

^{1/} The authors express appreciation to Mrs. M. B. Soniat for her direct collaboration in the overall planning, composition and writing of this report.

^{2/} In addition to turpentine the naval stores industry also produces 5 million drums (520 pounds each) of rosin from which additional useful chemicals with interesting composition can be obtained.

Based on preliminary tests, its properties and those of the derivatives prepared from the acid, suggest possible application in the following areas:

Adhesives:	Thermosetting--hot melts, etc.
Agricultural:	Plant hormones, pesticides, fungicides
Chemical:	Intermediate in synthesis of esters, amides, amine salts, vinyl monomers
Mechanical:	Lube and oil additives, cutting oils, greases
Plastics:	Plasticizers, polyester resins, epoxy resins, polymers
Rubber:	Antioxidant such as a curing aid
Textiles:	Mercerizing agent, catalyst, finishing agent, formaldehyde crosslinking agent
Miscellaneous:	Ingredients for paints, polishes, ion-exchange resins

ECONOMICS

Production costs for pinonic acid may range from 20 to 30 cents a pound for the ozonolysis procedure depending on the volume of the acid produced and the cost of ozone.

Permanganate oxidation of alpha-pinene offers the simplest process for the production of the acid and allows for the use of standard equipment. However, because of the large quantity of potassium permanganate required per pound of pinonic acid produced, production costs for this procedure may range from 65 cents to as much as \$1.20 a pound depending on the volume of the acid manufactured.

Capital investment for the production of the acid in quantities ranging from 500,000 to 2,000,000 pounds a year may range from \$300,000 to as much as \$1,000,000 depending on the process selected and the specifications set for the final product.

TOXICITY

The toxicity of pinonic acid has not been determined. However, no ill effects have been observed by personnel working with the acid.

SAMPLES

Samples are available on request from the Naval Stores Laboratory, Olustee, Fla., until such time as pinonic acid becomes available commercially.

ACCOMPLISHMENTS

Two practical processes are available for the commercial production of pinonic acid. USDA scientists have prepared a large number of its derivatives, which possess properties desirable for utility as plasticizers, textile agents, lubricants, plant hormones, and intermediates for the production of unusual polymers such as polyurethanes, polyvinyls, polyamides, polyesters as well as epoxy resins. Preliminary evaluation indicates that the derivatives prepared from pinonic acid warrant further consideration for these applications.

PROCESS

Pinonic acid can be made easily by the oxidation of alpha-pinene; for example, by ozonolysis or treatment of the hydrocarbon with permanganate:

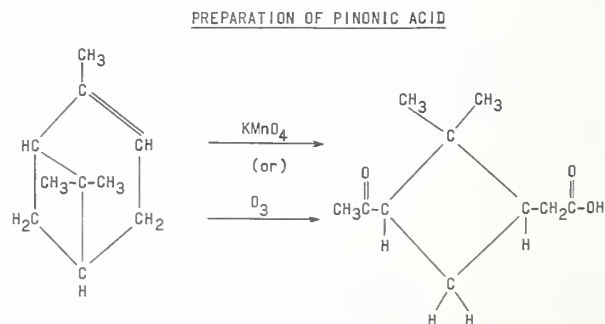


Figure 2. --Preparation of pinonic acid.

The acid is not being produced on a commercial scale in the United States. In view of the success achieved in the application of ozonolysis to the production of organic materials, it is somewhat surprising that low cost pinonic acid has not been produced by this simple and inexpensive process. Laboratory procedures for the conversion of alpha-pinene to the acid by ozonolysis produced the desired product in yields amounting to as much as 75 percent of theory. Pilot plant quantities of the acid were prepared at the Naval Stores Laboratory in Olustee, Fla. by the permanganate oxidation of alpha-pinene.

The procedure consisted of dissolving 18 pounds of ammonium sulfate in 10 gallons of water, followed by filtration to remove insolubles. The filtrate and 34 pounds of alpha-pinene were charged into a 100-gallon stainless steel reactor equipped for good agitation. Eighty pounds of potassium permanganate were gradually added during a 3-hour period to the mixture in the reactor while its contents were thoroughly stirred. The temperature of the batch during this addition was maintained at 5 to 10°C. by the addition of approximately 700 pounds of ice. The batch was allowed to remain in the reactor for approximately 12 hours before about one pound of solid sodium hydroxide was added to discharge the permanganate color. After filtration to remove manganese dioxide and thorough washing of the filter cake, the filtrate was returned to the cleaned reactor for extraction. Hydroxypinocampnone formed as a byproduct was removed first by several extractions with small portions of chloroform using approximately 20 gallons of the solvent for the entire operation. Acidification with dilute sulfuric acid results in precipitation of pinonic acid as an oil which crystallizes from the aqueous mixture as an almost colorless crystalline product. Because the organic acid is soluble in water, extraction of the filtrate with chloroform or benzene is recommended. For manual operation wherein only small quantities of the solvent are used per extraction, chloroform is a preferred solvent. However, for continuous

extraction, benzene can be used. In the pilot plant operation, several three-gallon portions of chloroform were used as the extractant. The extract was dried over anhydrous sodium sulfate before the solvent was removed by distillation. The quantity of crude product isolated amounted to 28 pounds or approximately 61 percent of theory. Crystallization from acetone yields a colorless product possessing the physical properties listed for pinonic acid in the literature.

MATERIALS AND EQUIPMENT

Chemicals required

alpha-Pinene--commercial grade
Ammonium sulfate--fertilizer grade
Potassium permanganate
Sodium hydroxide--technical grade
Sulfuric acid--technical grade
Chloroform or benzene

Oxidation

Equipment for the oxidation should be constructed of corrosion resistant material. Explosion proof motors and electrical fixtures are recommended. Provision should be made for efficient agitation. A suggested flow diagram follows.

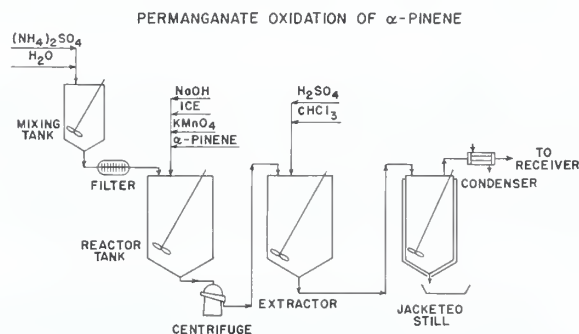


Figure 3. --Permanganate oxidation of alpha-pinene.

SCOPE OF INVESTIGATION

In the interest of brevity, only selected studies on the preparation of the acid and its derivatives and on potential applications will be described herein. Selected reactions of pinonic acid and its derivatives are listed in the diagram below. Further information on each phase can be obtained by contacting the key personnel listed in this manual.

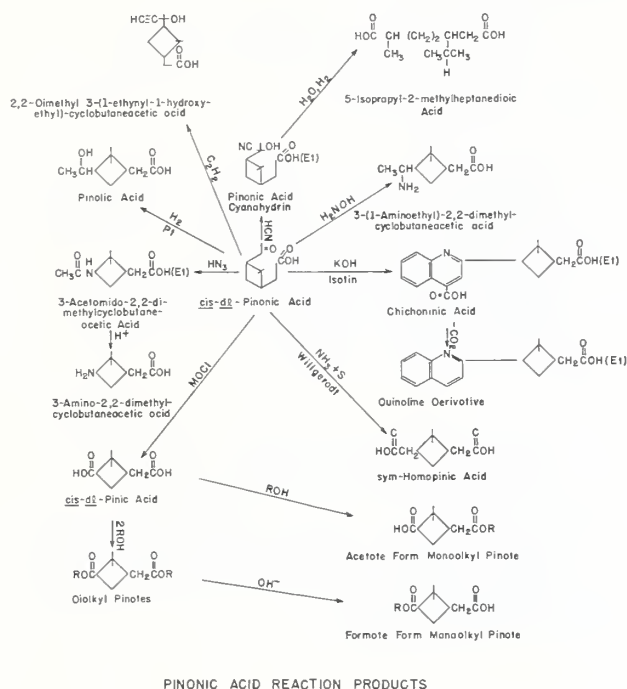


Figure 4. --Pinonic acid reaction products.

The effect on yields of pinonic and pinic acids by such variables as concentration of ozone reactant, ozone carrier, pinene solvent, and ozonization temperature were determined and reported in literature by the staff of the Armour Research Foundation.

Sodium sulfite as well as oxalic acid can be used in place of caustic to discharge the permanganate color.

Hydroxypinocamphone can be oxidized to pinonic acid by permanganate in a 5 percent sulfuric acid solution at 20°C. Over-all yields of the desired product, including the use of the byproduct, amount to about 75 percent.

KEY PERSONNEL INVOLVED ON PROJECT

Naval Stores Laboratory, Olustee, Fla.^{3/}

R. V. Lawrence

G. S. Fisher

G. W. Hedrick

Oilseed Crops Laboratory, New Orleans, La.^{3/}

L. A. Goldblatt

PUBLICATIONS AND PATENTS^{4/}

Publications

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^{3/} One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

^{4/} Reprints may be requested by reprint number.

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PREPARATION OF SOME MONO- AND DIALKYL PINATES FROM PINIC ACID.

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Patents

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PRODUCTION OF SYM-HOMOPINIC ACID. Stinson, J. S.; and Lawrence, R. V. U. S. Patent No. 2,765,334.

MERCERIZING COMPOSITIONS CONTAINING PINONIC ACID. Hedrick, G. W. U. S. Patent No. 2,974,002.

AMINO ACID CONTAINING A CYCLOBUTANE RING AND METHOD OF PREPARATION. Hedrick, G. W. U. S. Patent No. 3,005,842.

VINYL PINONATE AND POLYMERIC DERIVATIVES THEREOF. Hedrick, G. W. U. S. Patent No. 3,030,337.

AMINO ACIDS CONTAINING A CYCLOBUTANE RING. Hedrick, G. W. U. S. Patent No. 3,031,499.

VINYL CHLORIDE POLYMERS PLASTICIZED WITH HYDRONOPYL PINONATE. Hedrick, G. W.; and Magne, F. C. U.S. Patent No. 3,057,814.

ALKYL, ETHENYL ESTERS OF PINIC ACID AND POLYMERS THEREOF. Hedrick, G.W. U.S. Patent No. 3,063,970.

No patent warranties are hereby granted, implied, or otherwise made.

ADDITIONAL INFORMATION

Pinonic acid is another of many interesting and potentially valuable chemical intermediates developed in research at the Naval Stores Laboratory, Olustee, Fla. Others are listed below with pertinent reprint numbers.

Additional information on these and all developments of the Southern Utilization Research and Development Division are available on request from the laboratory in Olustee or from the Division headquarters in New Orleans. A list of Publications and Patents of the Division is published semiannually.

OTHER INTERESTING CHEMICALS FROM NAVAL STORES

Pinic Acid and Esters: Reprints No. 1049, 1125, 1185, 1213, 1215, 1642, 1673, 1761, 1850, 1916, 1945, and 2014.

Sym-Homopinic Acid: Reprints No. 1125, 1673.
Hydroxypinocamphone: Reprint No. 2014.

Pinolic Acid and Esters: Reprints No. 1216, 1989, 2304, and 2305.

Homoterpenylmethyl Ketone: Reprints No. 1612, 2014, and 2674.

Other Cyclobutaneacetic Acids: Reprints No. 1673, 1945, 2014, and 2674.

Levopimaric Acid: Reprints No. 1218, 1297, 1606, 1611, 1760, 1932, 2073, 2137, 2142, 2525, 2597, 2595, and 2732.

Pine Gum Peroxides: Reprints No. 1606, 1760, 1855, 1856, 1932, 2073, 2142, and 2732.

